

DETERMINATION OF BENZENE IN
COMMERCIAL GASOLINE

BY

RAYMOND K. SCHERGER

ARMOUR INSTITUTE OF TECHNOLOGY

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DETERMINATION OF BENZENE IN COMMERCIAL GASOLINE

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A THESIS

PRESENTED BY

RAYMOND K. SCHERGER

TO THE

PRESIDENT AND FACULTY

OF

ARMOUR INSTITUTE OF TECHNOLOGY

FOR THE DEGREE OF

BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

MAY 31, 1921

APPROVED:

H. McCormack
Professor of Chemical Engineering

H. M. Raymond
Dean of Engineering Studies

L. C. Mohr
Dean of Cultural Studies

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Table of Contents.

	Page
Object	1
Method to be followed	2
Bromination of toluene and xylene	
With iron	7
Without a catalizer	10
With iron and water	12
Conclusion	15
Tables	19
Bibliography	30

The object of this work is to determine to what extent toluene and the xylenes will brominate in the presence of a catalizer, and also to determine what are the ultimate compounds formed when toluene and xylene are brominated in sunlight without a catalizer. This is to be done in order to know what happens to toluene and xylene when bromination occurs in the presence of benzene, gasoline and a brom carrier.

A method for the determination of benzene in mixtures of benzene and paraffines by bromination has been worked on and found to be successful. The method, however, is to be used to determine benzene in commercial gasoline, and in the lighter distillates of petroleum. Petroleum distillates contain varying quantities of gasoline, kerosene, benzene, toluene, xylene, and a few double bond hydrocarbons.

Therefore, in order to find if the method prescribed is applicable it is necessary to know what will happen to these olefine hydrocarbons when bromination takes place in their presence.

Inasmuch as this subject has been treated before in the thesis of Wm. Mendius and W. T. McCauley, it will not be necessary to summarize any of the previous work done in this line except that done by Mendius and McCauley, since their work will be used as a basis for this thesis.

The method for the determination of benzene in mixtures of benzene and paraffine as evolved by Mendius is as follows:

The specific gravity of the oil to be tested is determined and .1 cc. or about .1 gram of it is introduced into the clean and dry test bottle, which already contains the .02 gram of pure, 200 mesh iron. The author recommends the use of an ordinary ground glass stoppered bottle. Just enough carbon bisulphide is then added to dissolve the oil, say about 5 cc. Enough normal bromine solution is added to furnish the bromine for the iron

(.0579 gm. Br.), and the bromine to form the dibrombenzene (.360 grams. Br.) assuming the oil to be pure benzene. This is to furnish sufficient excess of bromine. The bottle is immediately stoppered, water sealed and let stand for one hour at 35° C. A blank test should be made with every series of tests to standardize the bromine solution. At the end of one hour the flask is cooled, the stopper removed and washed, and an excess of potassium iodide solution added.. The mixture is thoroughly agitated. The free iodine which was liberated by the equivalent amount of bromine not absorbed is titrated with a 1/5th normal solution of sodium thiosulphate, using starch solution to aid in the detection of the end point, which is the final disappearance of blue color. Much agitation is necessary. Knowing the standard and relationship of the two solutions, the amount of the bromine absorbed is calculated. This is the difference between the amount of bromine solution used and the brom-equivalent of the thiosulphate solution, times the standard of the bromine solution. The amount of bromine reacting with the iron is subtrated from this. The resulting figure is the amount of bromine absorbed by the benzene. This is divided by 4.094, which gives the weight of benzene in the oil, With this data the percentage, by weight, of benzene in the oil can easily be calculated.

McCauley verified the results obtained by Mendius and found the method he used to determine benzene in paraffines to be accurate and fairly rapid. McCauley ran several tests on mixtures of benzene and gasoline and found that the method gave good results. He also tried various brom carriers to substitute for the iron with the view of making the method more rapid. The iron, however, gave the most satisfactory results. The method of procedure was left unchanged, remaining precisely as Mendius had planned it.

The first problem coming to mind when dealing with commercial mixtures of gasoline, benzene, toluene and xylene, such as we find, in some motor fuels is, what will happen to the toluene and xylene when treated with bromine in exactly the same manner as the benzene is treated in the above determination? The bromine solution to be used for this

purpose is to be a normal solution in freshly distilled carbon bisulphide. It is very important that the carbon bisulphide be perfectly free from water and recently distilled. The solution must be standardized about once every two days, since its bromine value would change considerably on standing.

To standardize the bromine solution use a 10 cc. sample. Put it in an Erlenmeyer flask, add water and potassium iodide solution in excess of that required to react with the bromine present. Titrate with 1/5th normal sodium thiosulphate solution.

The N/5 thiosulphate solution is made by dissolving 49.664 grams. of pure sodium thiosulphate in 1000 cc. of distilled water.

To standardize the thiosulphate solution weigh out 4.903 grams of pure dry potassium dichromate and dissolve in one liter of water. A measured amount of this solution is added to the acid solution containing about 3 grams of potassium iodide and 10 cc. of

strong hydrochloric acid. The solution is diluted with 500 cc. of water, for here the color change is not from blue to colorless, but from blue to light green. Titrate with the prepared thiosulphate solution. From the weight of potassium dichromate reacted with calculate the standard of the sodium thiosulphate solution.



The Bromination of Toluene and Xylene With Iron.

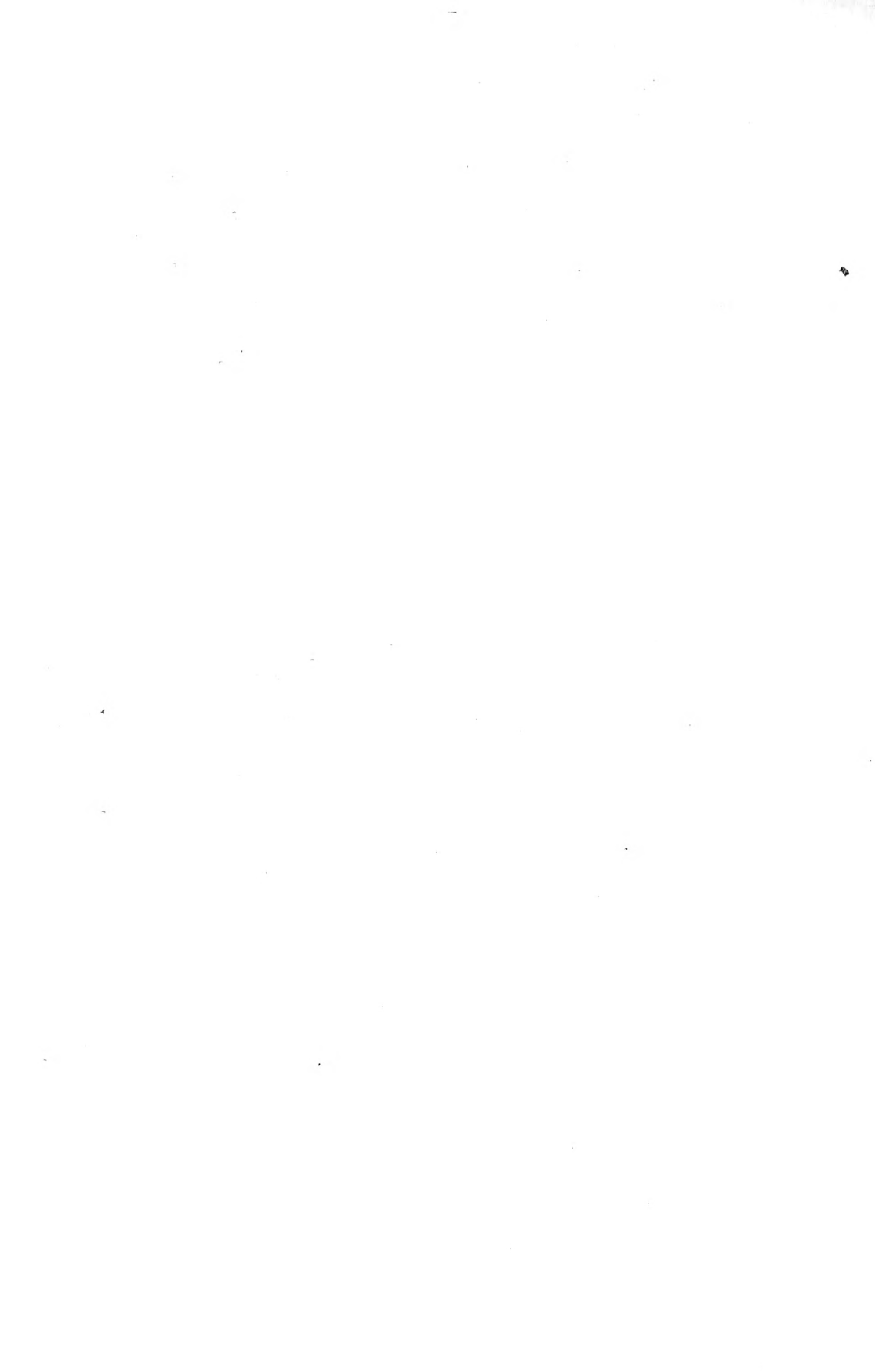
The bromination product of xylene and toluene was determined by treating 1/10th cc. of the pure substance in the same manner as benzene is treated in the prescribed way, namely:

The specific gravity of the xylene or toluene to be tested is determined and 1/10th cc. or about .1 gram of it is introduced in a clean and dry test bottle, which already contains .02 grams of pure 200 mesh iron. Just enough carbon bisulphide is then added to dissolve the oil, say about 5 cc. Enough normal bromine solution is then added to furnish the bromine for the iron (.0579 gram Br.), and the bromine to form dibromtoluene and xylene (toluene requires .2808 gram bromine - xylene required .2594 grams. bromine to form the dibrom compound.

Many samples of toluene and xylene were

run according to this procedure, the results being shown in tables 1 and 2. From the results is it evident that the dibrom compound is formed in both cases. The method of taking samples and adding bromine solution were rather poor, consequently the results are not as accurate as they might be, nevertheless the results are constant enough to show that the dibrom and nothing but the dibrom compound was formed. A number of runs were made in the cold (temperature 15° C.), and the bromination was found to be the same as when the temperature was around 35° C. The same applies to benzene. The all important item is that absolutely no water should be present during the bromination and, that the carbon bisulphide used for the bromine solution should be freshly distilled.

The conclusion drawn from these results is that toluene and xylene will brominate to form the dibrom compound in the presence of



an iron catalizer at ordinary temperatures, the bromine attaching itself to the ring. We know, from the work done by Mendius that benzene will brominate under the same conditions also to form the dibrom compounds, and that gasoline and other single bond paraffines will not brominate at all. Therefore, if we have gasoline, benzene, toluene and xylene in a mixture, and if we brominate the mixture the toluene, benzene and xylene will all come down as the dibrom compound and the gasoline will not brominate at all. In this way we can approximate the percentage of the mixture of benzene, toluene and xylene, but in order to know the percentage of benzene alone we must devise a method for the determination of xylene and toluene in the presence of benzene and gasoline.

Without a Catalizer.

Toluene ($C_6H_5CH_3$) and xylene ($C_6H_4CH_3CH_3$) differ from benzene (C_6H_6) in that they have a side chain consisting of one methyl group in the first case and two methyl groups in the second. We know from our organic chemistry that when bromination takes place in the presence of a brom carrier the bromine goes on the ring and not on the side chain. We also know that if we brominate in sunlight, and in the absence of a brom carrier, the bromine will attach itself to the side chain rather than the ring. It is to be expected that, since benzene has no side chain, bromination would not take place without catalizer, and the bromination will take place in the case of toluene and xylene without a catalizer in the presence of sunlight. Consequently numerous samples of benzene, toluene and xylene were set up for bromina-



tion in sunlight and without any iron. The results of this test are shown in tables, 3, 4, and 5.

From the results it is plain that there is no bromination in the case of benzene and that the degree of bromination in the case of toluene and xylene depends upon the time. However, it was found that the strength of the sunlight also affected the bromination, therefore, we have two variables to content with, namely, time and light. Moreover bromination does not seem to stop at any definite place. It approaches total bromination of the side chain, but very seldom reaches it. When the higher bromo compounds are formed they decompose easily and consequently it is impossible to get a definite end point during titration. For these reasons bromination in sunlight without a catalizer was abandoned.

With Iron and Water.

It was noticed that when a few drops of water was present bromination of benzine with a catalizer was seriously impaired. It was not known how water affected the bromination of toluene and xylene, and, therefore, several tests were made to determine this. Five CC. of water were added to samples of benzene, toluene and xylene along with iron and enough bromine in a carbon bisulphide solution to form the dibrom compound in each case. The samples were allowed to stand in subdued light at ordinary temperatures for about one hour. The results as shown in tables 6, 7, and 8 were very promising. They showed that in the case of benzene just enough bromine was absorbed to react with the .02 grams of iron (.0579 gms. bromine), and that the benzene itself was left unbrominated. The xylene required enough bromine to satisfy the iron and to

form the tri-brom compound. The toluene required enough bromine to react with the iron and to form the dibrom compound.

We conclude from this that the benzene does not brominate when water is present even though a catalizer is there, whereas toluene and xylene do brominate when water and a catalizer are present to form the dibrom and tri-brom compounds respectively. Inasmuch as we may not know the amounts of xylene and toluene present and have no way of finding out it will be necessary to average the amount of bromine needed to brominate equal amounts of toluene and xylene, and thus treat the two as one compound, a gram. of which will require .3995 grams. bromine.

1 gm. xylene requires 4.515 gm. br. to form the tri-brom compound.

1 gm. toluene requires 3.476 gms. Br. to form the dibrom compound.

1/2 gm. toluene plus 1/2 gm. xylene requires 3.995 gms. bromide to brominate the mixture.

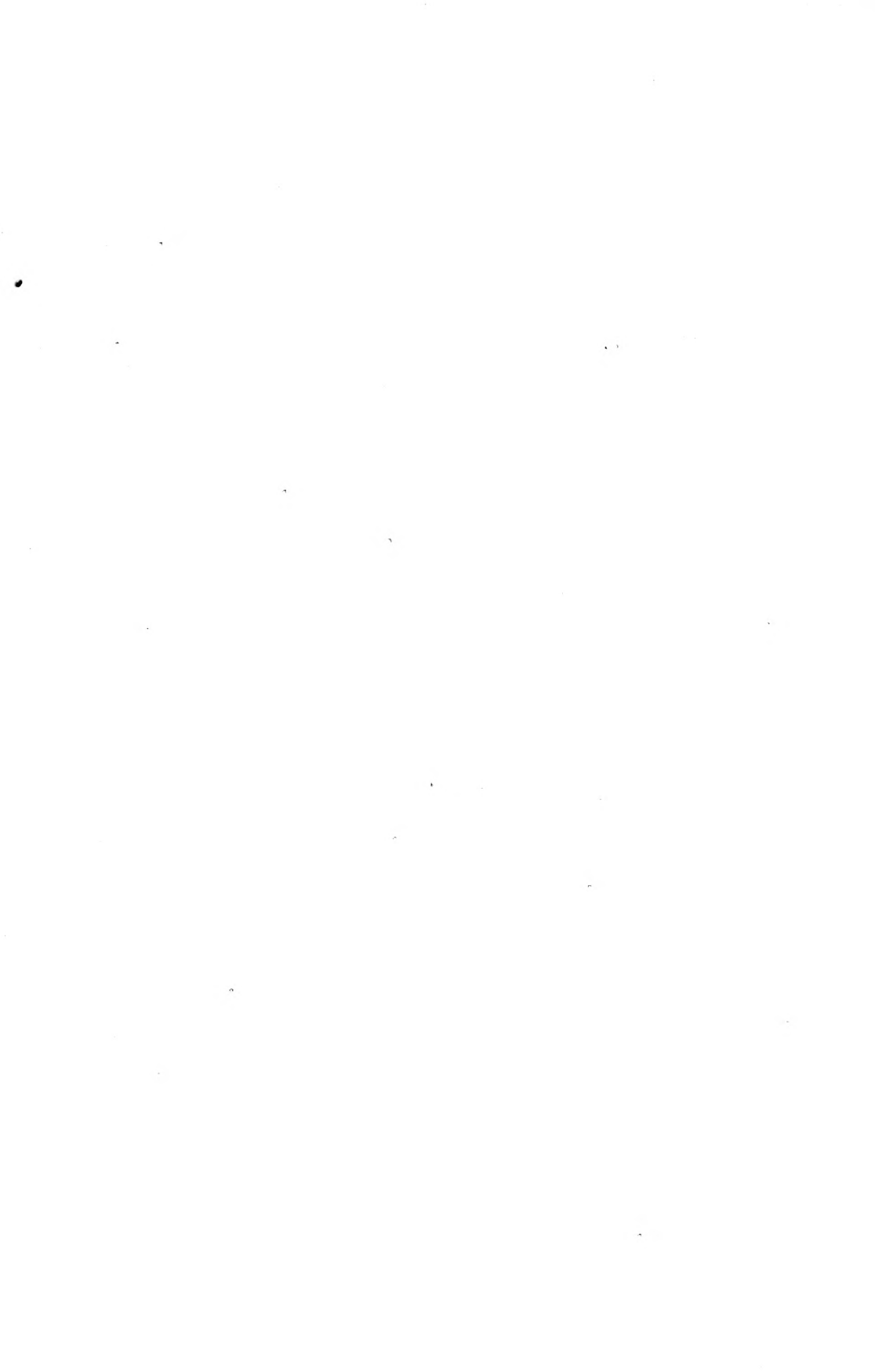
The best results are obtained when an excess of bromine is present and the time is about one and one-half hours. It is only necessary to add a small amount of water, approximately 5 cc. The time did not permit to investigate whether or not the bromine attached itself to the side chain or to the nucleus, but nevertheless in all cases a definite compound was formed and not a mixture of compounds as when the toluene and xylene were brominated in sunlight free from water.

CONCLUSION.

The method for the determination of benzene in mixtures of benzene, gasoline, toluene and xylene will require two separate determinations, first the determination of toluene and xylene, second the determination of toluene, xylene and benzene. It is as follows:

The specific gravity of the oil to be tested is determined in 1/10th cc. or about 1/10th gram of it is introduced into a clean ground glass stoppered bottle, which already contains .02 grams of 200 mesh C.P. iron enough normal bromine solution is added to furnish the bromine for the iron (.0579 grams Br.), and the bromine to brominate the oil (.4515 grams Br.), assuming the oil to be pure toluene since toluene requires the most bromine to be satisfied. This is to furnish sufficient excess of bromine. Introduce about 5 cc. of water into the bottle,

stopper it and allow it to stand in subdued light for one and one-half hours. A blank test should be made every series of test to standardize the bromine solution. At the end of one and one-half hours the stopper is removed and washed, and an excess of potassium iodide solution is added. The mixture is thoroughly agitated. The free iodine which was liberated by the equivalent amount of bromine not absorbed, is titrated with 1/5th normal solution of sodium thiosulphate, using starch solution to aid the detection of the end point, which is the final disappearance of blue color. Much agitation is necessary. Knowing the standard and relationship of the two solutions the amount of bromine absorbed is calculated. The difference between the amount of solution added and the brom equivalent of the thiosulphate solution times the standard of the bromine solution gives the amount of bromine absorbed. The grams of bromine reacting with



the iron is subtracted from this. The final result will be the amount of bromine necessary to react with the toluene and xylene present. To get the weight of a mixture of toluene and xylene in the oil, divide the grams of bromine by 3.995. From this result knowing the weight of the sample the percentage of the mixture of toluene and xylene is calculated.

To find the amount of benzene in the oil go through the analysis as prescribed by Mendius. Subtract from the final amount of bromine necessary to brominate the oil, the amount of bromine used in the above determination and divide the result by 4.094.

This will give the weight of benzene in the oil. From this and the weight of the sample the percentage of benzene is easily calculated.

In pure mixtures of toluene and xylene are brominated with water and a catalizer according to the method prescribed, a certain bromine absorbtion will take place. The gram value of this absorbtion will be greater in the case of xylene than in the case of toluene, since a unit weight of xylene absorbs more bromine than a unit weight of toluene in the ratio of .4515 to .3476. This means that one gram of pure xylene will absorb 4.515 grams. of Br. and that one gram of pure toluene will absorb 3.476 grams of Br. One gram samples of all mixtures of the two will absorb a definite amount of bromine the value of which will lie between 4.515 and 3.476. Therefore, it is possible to make a table or to draw a curve which will give percentages of toluene and xylene from the bromine value of a certain sample. Such a table and curve is included herein.

TABLES.

TABLE I.

Bromination of Xylene with iron catalizer.

Sample	Br Absorbed	Bromine necessary for dibrom comp.	% Error
1	.2673	.2594	3.0
2	.2920	"	8.2
3	.2689	"	3.2
4	.2502	"	1.2
5	.2600	"	2.9
6	.2730	"	5.0
7	.2589	"	.0

TABLE II

Bromination of Toluene with iron catalizer.

Sample	Br. absorbed	Bromine necessary for dibrom comp.	% Error
1	.3203	.2808	13.0
2	.3109	"	10.4
3	.3129	"	11.3
4	.3030	"	7.0
5	.2912	"	3.0
6	.2943	"	3.3
7	.3021	"	6.9
8	.2734	"	6.0
9	.3043	"	7.2

TABLE III.

Benzene, Without Iron, In Sunlight.

Sample	Gr. Benzene	Br. Bromine Present	Gr. Bromine Absorbed
1	.0850	.4860	.0200
2	"	"	.0030
3	"	"	.0096
4	"	"	.0011
5	"	"	.0009
6	"	"	.0010
7	"	"	.0008
8	"	"	.0083

TABLE IV.

Toluene, In Sunlight, Without Iron.

Sample	Grms. Toluene	Gr. Br. Present	Gr. Br. Abs.	Time
1	.08647	.4860	.0320	5
2	"	"	.0560	10
3	"	"	.0920	15
4	"	"	.0930	20
5	"	"	.1240	20
6	"	"	.1120	30
7	"	"	.1630	30
8	"	"	.2640	60
9	"	"	.3242	2 hr.
10	"	"	.4326	3 hr.

TABLE V.

Xylene, Without Iron, In Sunlight.

Sample	Gms. Xylene	Gr. Bromine Present	Gr. Br. Abs.	Time
1	.08589	.4860	.0832	10 min.
2	"	.4860	.0993	15 "
3	"	.4860	.1297	20 "
4	"	.4860	.1340	20 "
5	"	.4860	.1302	20 ""
6	"	.4860	.1920	20 "
7	"	.4860	.2232	30 "
8	"	.4860	.2920	40 "
9	"	.4860	.3212	60 "
10	"	.7530	.6520	2 Hr.
11	""	.7530	.5320	4 "
12	"	.7530	.6102	4 "

TABLE VI.

Bromination of benzene in present of water
and iron.

Sample	Gm. Benzene	Gm. Br. Present	Total	Gm. Br. By iron	Abs. By Benzene
1	.08500	.4860	.0580	.0579	.0001
2	"	"	.0592	"	.0013
3	"	"	.0590	"	.0001
4	"	"	.0593	"	.0001
5	"	"	.0620	"	.0015
6	"	"	.0540	"	.0000
7	"	"	.0572	"	.0000
8	"	"	.0593	"	.0014
9	"	"	.0584	"	.0005
10	"	"	.0572	"	.0000

TABLE VII

Bromination of Toluene in presence of
water and iron.

Sample	Gm. Toluene	Gm.Br. Present	Gm.Br req.	Gm. Br. Abs.	% Error
1	.1000	.4860	.3476	.3320	5.0
2	"	"	"	.3360	3.0
3	"	"	"	.3420	.91
4	"	"	"	.3224	7.0
5	"	"	"	.3446	.72
6	"	"	"	.3390	2.9
7	"	"	"	.3424	.89
8	"	"	"	.3296	6.6
9	"	"	"	.3420	.91
10	"	"	"	.3417	.90

TABLE VIII

Bromination of Xylene in presence of
water and iron.

Smple	Gm. xylene	Gm.Br. Present	Gm. Br. req.	Gm. Br. Abs.	% Error.
1	.1000	.4860	.4515	.4002	-11.2
2	"	"	"	.4012	-11.0
3	"	"	"	.4423	.2
4	"	"	"	.3920	-13.5
5	"	"	"	.4230	-6.2
6	"	"	"	.4360	-3.1
7	"	"	"	.4200	-6.7
8	"	"	"	.4195	-3.5
9	"	"	"	.4093	-10.3
10	"	"	"	.4162	-8.7

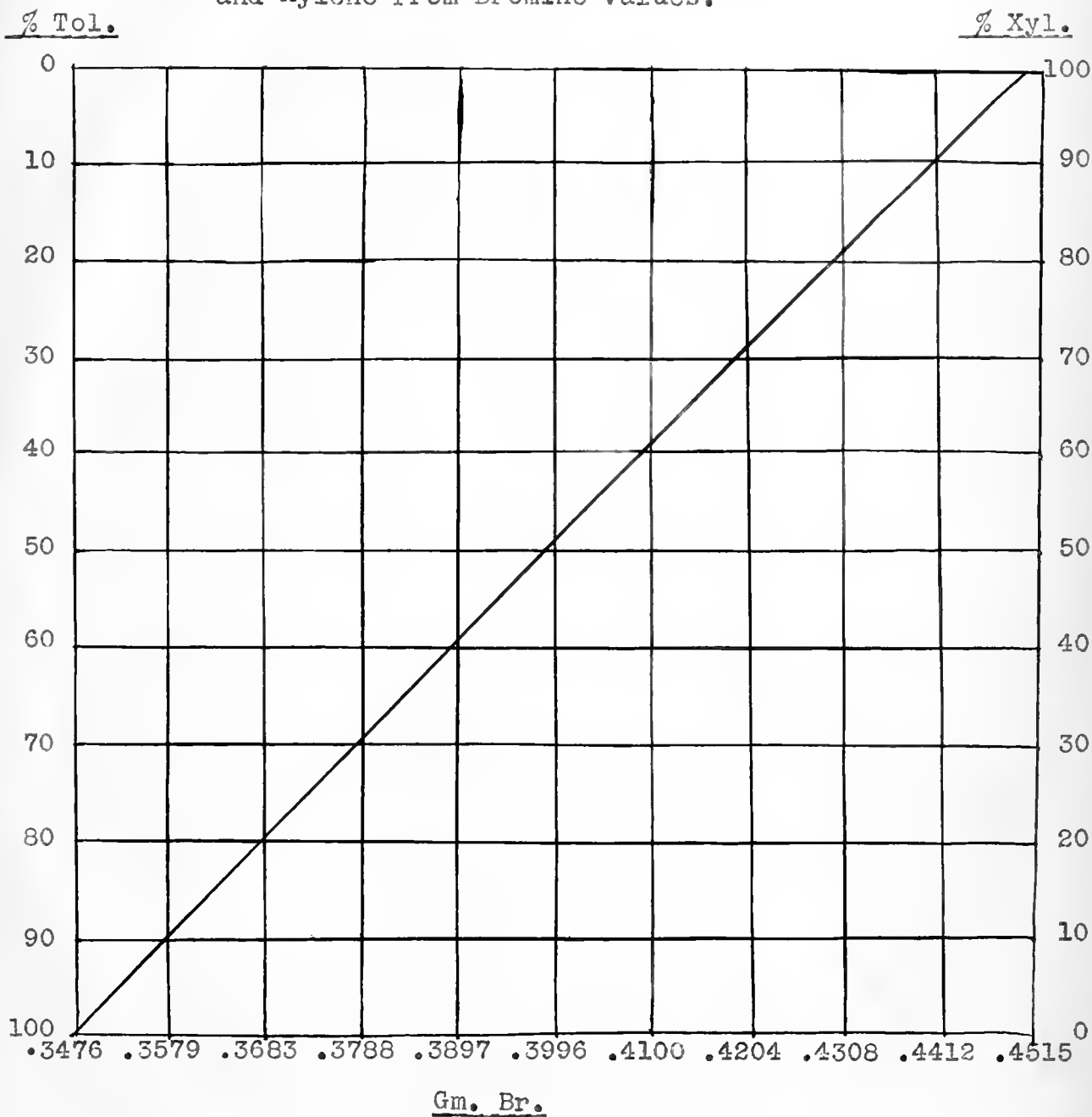
TABLE IX

For pure mixtures of Toluene and Xylene.

. 1 gm. sample of mixture.

Gm. Toluene	Gm. Xylene	Gm. Br.	% Toluene	% Xylene
.10	.00	.3476	100	0
.09	.01	.3479	90	10
.08	.02	.3683	80	20
.07	.03	.3787	70	30
.06	.04	.3891	60	40
.05	.05	.3995	50	50
.04	.06	.4099	40	60
.03	.07	.4213	30	70
.02	.08	.4307	20	80
.01	.09	.4411	10	90
.00	.10	.4515	0	100

Graph showing the percentages of Toluene
and Xylene from Bromine values.



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